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 CLAIMS

[Claim(s)]

[Claim 1] It is the electrolytic solution for lithium rechargeable batteries which is the electrolytic solution containing a high dielectric constant solvent and a hypoviscosity solvent for lithium rechargeable batteries, and is characterized by the bird clapper from the organic fluoridation ether compound in which the above-mentioned hypoviscosity solvent is shown by a following formula (** 1) or (** 2) a following formula.

R1-O-R1 (** 1)

R1-O-R2 (** 2)

((As for R1 in a formula (** 1) and (** 2) a formula, the fluoridation alkyl group or carbon atomic number of 1-10 expresses the fluoridation alkyl group of 1-10.) However, as for R2, a carbon atomic number expresses [a carbon atomic number] the alkyl group of 1-10.)

[Claim 2] For R2, the fluoridation alkyl group or carbon atomic number of 1-5 is the electrolytic solution for lithium rechargeable batteries to which the carbon atomic number of R1 in a formula (** 1) or (** 2) a formula is the fluoridation alkyl group of 1-5, and a carbon atomic number is characterized by the bird clapper in a claim 1 from the organic fluoridation ether compound with which it has the alkyl group of 1-5.

[Claim 3] It is the electrolytic solution for lithium rechargeable batteries characterized by the bird clapper from the organic fluoridation ether compound in which an organic fluoridation ether compound is shown by the following formula (** 3) in a claim 1 or a claim 2.

CF₃-CH₂-O-CH₂-CF₃ (** 3)

[Claim 4] The electrolytic solution for lithium rechargeable batteries which prepares the mixing ratio of a high dielectric constant solvent and a hypoviscosity solvent in the range of 90:10 or 20:80, and is characterized by the bird clapper in the electrolytic solution for lithium rechargeable batteries of a claim 1 or a claim 3 given in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention is stable, without causing oxidative degradation in the voltage range which starts the nonaqueous electrolyte for lithium cells, especially exceeds 4V in a lithium rechargeable battery, and relates to the nonaqueous electrolyte for lithium rechargeable batteries which has high conductivity also in a low temperature field 0 degree C or less.

[0002]

[Description of the Prior Art] The cell which has the developed high-energy density recently consists of the alkali-metal matter as a negative-electrode active material, a transition-metals chalcogen compound as a positive active material, and the organic electrolytic solution as the electrolytic solution. Also in this cell, use a lithium or a lithium content alloy as a negative electrode, and transition-metals chalcogen compounds, such as manganese dioxide or a vanadium pentoxide, are made into a positive active material. The chemical cell using what dissolved alkali-metal salts, such as a lithium perchlorate and a 6 fluoride [phosphoric-acid] lithium, in organic solvents, such as a propylene carbonate or a tetrahydrofuran, or these mixed solutions as an electrolyte as the organic electrolytic solution Since a lithium is an element with the smallest specific gravity with the largest and ionization tendency also in all metallic elements, there is the feature that the energy per unit weight serves as the maximum. Furthermore, the point that electric discharge and charge are repeatedly possible as an important feature of these chemical cells is mentioned. Indicating [and] that high ion conductivity can take out big current as the organic electrolytic solution used for this chemical cell, it is a well-known fact that it must be hypoviscosity. Conventionally, it uses in many cases combining the high dielectric constant solvent and hypoviscosity solvent in which high electrolyte solubility is shown as an organic solvent for the electrolytic solutions which satisfies this condition. As a typical thing used as a high dielectric constant solvent, a propylene carbonate, an ethylene carbonate, gamma-butyrolactone, dimethyl sulfoxide, the sulfolane, the acetonitrile, etc. are known, for example. A tetrahydrofuran, dimethoxyethane, the dioxolane, etc. are known as a typical thing used as a hypoviscosity solvent. The electrolytic solution prepared using these organic solvents shows high ion conductivity, and since it is hypoviscosity, it has the feature that the transference number of ion is large. Therefore, when it considers as a cell, electric capacity increases and it is thought that the chemical cell in which high current electric discharge is possible can be realized. Here, if the requirement as an organic solvent for the electrolytic solutions is arranged, dissolve (1) electrolyte by high concentration.

- (2) Fully carry out ionic dissociation of the dissolved electrolyte.
- (3) Have a high oxidation potential.
- (4) It is hypoviscosity. The conditions of ** are needed. Although the above-mentioned solvent used as a high dielectric constant solvent satisfies the above-mentioned conditions (1), (2), and (3), and it is a high dielectric constant therefore, the conditions of the above (4) must have been satisfied in essence. Although use of a hypoviscosity solvent is needed in order to compensate this fault, the above-mentioned hypoviscosity solvent used from the former cannot satisfy the conditions of the above (3).

That is, the organic solvent for the conventional electrolytic solutions was not fully stable, when it was used for the lithium rechargeable battery using the positive-electrode material which the low thing of the own oxidation potential of a hypoviscosity solvent becomes a cause, for example, exceeds 4V, and while repeating charge and discharge, the solvent caused oxidative degradation gradually, and it had a problem of the ability not to make a long-term charge-and-discharge cycle life realize. In addition, in JP,1-117838,A, the proposal of the ** fluorine alkoxy ethane used as an electrolytic-solution solvent of a lithium cell is made as conventional technology.

[0003]

[Problem(s) to be Solved by the Invention] As mentioned above, when the conventional electrolytic solution for lithium cells was used for a cell with the voltage beyond 4V, there was a problem that the charge-and-discharge SAIRUKU life as a cell became short.

[0004] The purpose of this invention is very stable, and hypoviscosity shows high ion conductivity under a low temperature service, the trouble in the above-mentioned conventional technology is canceled, and oxidative degradation is not caused in the voltage range exceeding 4V, but they are [it has few falls of cell capacity and] to offer the nonaqueous electrolyte for lithium rechargeable batteries with a long charge-and-discharge cycle life.

[0005]

[Means for Solving the Problem] in order to attain the purpose of the above-mentioned this invention -- as a hypoviscosity solvent -- a group -- the nonaqueous electrolyte containing the organic solvent which consists of an organic fluoridation ether compound for lithium rechargeable batteries is used this invention is nonaqueous electrolyte containing a high dielectric constant solvent and a hypoviscosity solvent for lithium rechargeable batteries, and the organic fluoridation ether compound shown by a following formula (** 1) or (** 2) a following formula as the above-mentioned hypoviscosity solvent is used for it.

R1-O-R1 (** 1)

R1-O-R2 (** 2)

R1 [however,] in a formula (** 1) and (** 2) a formula -- a carbon atomic number -- the fluoridation alkyl group of 1-10 -- as for R2, the fluoridation alkyl group or carbon atomic number of 1-10 expresses [a carbon atomic number] the alkyl group of 1-10 By using the organic fluoridation ether compound shown by an above-mentioned formula (** 1) or (** 2) an above-mentioned formula as a hypoviscosity solvent of the electrolytic solution for lithium rechargeable batteries It is stable, without causing oxidative degradation also in the voltage range exceeding 4V, and hypoviscosity can show high ion conductivity under a low temperature service, and there are few falls of cell capacity and they can realize the long lithium rechargeable battery of a charge-and-discharge cycle life. Since the viscosity as a hypoviscosity solvent will be increased, the ion conductivity in low temperature (0 degree C or less) will decrease and a cell property will fall if the carbon atomic number exceeds 10, the fluoridation alkyl group and alkyl group in the organic fluoridation ether compound shown by the above-mentioned (** 1) formula and (** 2) the formula are not desirable. And the more desirable range is an organic fluoridation ether compound with which a carbon atomic number contains the fluoridation alkyl group or alkyl group of the range of 1-5. R1 set which constitutes the organic fluoridation ether compound (R1-O-R1) shown by the formula (** 1) of this invention It is the basis which replaced with the fluorine the one section or all of hydrogen of the alkyl group shown by C_nH_{2n+1} -, and fluoridation alkyl groups, such as CF_3 -, CF_3CH_2 -, $CF_3(CH_2)$ (2-9)-, and $CF_3(CF_2)$ (2-9)-, are specifically mentioned. Moreover, R2 set which constitutes the organic fluoridation ether compound (R1-O-R2) shown by the formula (** 2) is a basis shown by above-mentioned C_nH_{2n+1} -, and the alkyl group specifically shown by CH_3 -, $CH_3(CH_2)$ (1-9)-, etc. is mentioned. An organic fluoridation ether compound desirable as a hypoviscosity solvent of this invention is the screw (2, 2, and 2-TORIFURORO ethyl) ether compound shown by the following formula (** 3), and $CF_3-CH_2-O-CH_2-CF_3$ (** 3)

Or n-butyl - 1, 1, 2, and 2-tetrapod FURORO ethyl ether, 2, 2, 3, 3, and 3-pen TAFURORO propylmethyl ether, 2, 2 and 3, 3-pen TAFURORO propyl - 1, 1, 2, and 2-tetrapod furol ethyl ether, A 1, 1, 2, and 2-tetrapod FURORO ethyl methyl-ether, 1, 1 and 2, and 2-tetrapod FURORO ethyl ethyl ether

or 1, 1, 3 and 3, and 3-pen TAFURORO-2-TORIFURORO methylpropyl methyl ether etc. is mentioned.

As a hypoviscosity solvent of the nonaqueous electrolyte containing the high dielectric constant solvent and hypoviscosity solvent of this invention for lithium rechargeable batteries a group mentioned above - the lithium cell using the nonaqueous electrolyte containing an organic fluoridation ether compound for lithium rechargeable batteries Since the rapid decline in conductivity is not seen [in / low temperature (0 degree C or less) / the oxidative degradation potential of the above-mentioned hypoviscosity solvent is high, and] It can be stabilized and used also in the high voltage range exceeding 4V, and a low-temperature property also has the feature that it is good, charge-and-discharge efficiency is also high, and the charge-and-discharge property of a longevity life is acquired.

[0006]

[Function] An organic fluoridation ether compound decreases the electron density on an oxygen atom for the strong electronegativity of a fluorine atom, and has the work which prevents drawing out the electron from a molecule. Specifically compared with the ether compound which consists of usual carbon, hydrogen, and oxygen, no less than about 2.0-2.5eV of ionization potentials of an organic fluoridation ether compound becomes large. Therefore, when an organic fluoridation ether compound is used as a solvent of the electrolytic solution, an electron is not drawn out in an interface with the positive active material of a high-voltage system with the strong oxidation, and oxidative degradation becomes is hard to be carried out. Furthermore, in low temperature, since there are few falls of ionic conductivity, the feature at the time of using these organic fluoridation ether compounds for the solvent of the electrolytic solution is in the place which can take out current with them also in low temperature 0 degree C or less. [there are few falls of cell capacity and big] That is, since viscosity rose rapidly while temperature falls, the ion conductivity in low temperature decreased and the conventional organic solvent had the problem that a cell property fell. On the other hand, since rapid elevation of viscosity does not arise even if temperature falls, the electrolytic solution containing the organic fluoridation ether compound of this invention has the feature that a cell property does not fall in low temperature. As an example of the organic fluoridation ether compound of this invention, as mentioned above For example, the screw (2, 2, and 2-TORIFURORO ethyl) ether, n-butyl - 1, 1, 2, and 2-tetrapod FURORO ethyl ether, 2, 2, 3, 3, and 3-pen TAFURORO propylmethyl ether, 2, 2 and 3, 3-pen TAFURORO propyl - 1, 1, 2, and 2-tetrapod furol ethyl ether, Although a 1, 1, 2, and 2-tetrapod FURORO ethyl methyl-ether, 1, 1 and 2, and 2-tetrapod FURORO ethyl ethyl ether or 1, 1, 3 and 3, and 3-pen TAFURORO-2-TORIFURORO methylpropyl methyl ether etc. is mentioned Although it is also possible to use each above-mentioned hypoviscosity solvent independently when preparing the electrolytic solution, using the organic fluoridation ether compound of these series as a hypoviscosity solvent, you may mix and use two or more sorts of solvents. It is also possible to add and use for these organic fluoridation ether compounds the organic solvent which consists of other carbon, hydrogen, and oxygen and which is generally used further again. However, independent [which carried out in this way and was prepared], or the hypoviscosity solvent of a mixed stock cannot be used as the electrolytic solution, if the solubility of supporting electrolytes, such as LiPF₆ and CF₃SO₃Li, is low and remains as it is. As ether which contains a fluorine in a molecule, although ** fluorine alkoxy ethane which is proposed in JP,1-117838,A is known, in this, the organic fluoridation ether compounds of this invention completely differ structurally, for example. Moreover, there is no publication about the physical properties of the electrolytic solution of the lithium cell which dissolved and prepared the supporting electrolyte to ** fluorine alkoxy ethane in the above-mentioned open official report, and it does not have even suggestion. Although the electrolytic solution of this invention mixes the above-mentioned hypoviscosity solvent to the above-mentioned high dielectric constant solvent, and the supporting electrolyte which becomes this mixed solvent from an alkali-metal salt is dissolved and being considered as the organic electrolytic solution, as for the mixing ratio of a high dielectric constant solvent and a hypoviscosity solvent, it is desirable that it is the range of 90:10 to 20:80. The reason is that only low ionic conductivity is too shown since a supporting electrolyte does not dissolve by high concentration that the viscosity of the electrolytic solution is high in a hypoviscosity solvent being 10% or less, and sufficient ionic conductivity is not obtained, and it is 80% or more. moreover, as the above-

mentioned supporting electrolyte LiClO_4 , LiAsF_6 , LiBF_4 and LiAlCl_4 which are generally known, LiCF_3CO_2 , LiNbF_6 , LiPF_6 , LiSbF_6 and LiTaF_6 , LiCF_3SO_3 , $\text{LiC}_6\text{F}_5\text{SO}_3$, $\text{Li}-\text{C}_4\text{F}_9\text{SO}_3$, and $\text{Li}-\text{C}_4\text{F}_9\text{SO}_3$ -- $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$, $\text{Li}(\text{CF}_3\text{SO}_2\text{N})_2$, KSCN , KI , LiCl , LiBr , etc. can be used.

[0007]

[Example] The example of this invention is given to below and it explains to a detail further using a drawing. To 100ml of propylene carbonates, beforehand, at 400 degrees C, 15g, in addition after agitating on the 1st, moisture was fully removed for the molecular sieve (type 4A) heat-treated for 4 hours through the activity alumina column. 5.32g of electrolytes LiClO_4 was dissolved in 50ml of this electrolytic-solution solvent, and the organic electrolytic solution of 1 mol concentration was prepared. Here, moisture was again removed for the organic electrolytic solution which could add screw (2, 2, and 2-TORIFURORO ethyl) ether 50ml, and was agitated through the activity alumina column. The relation between the voltage (V) when sweeping voltage by 0.1 mV/sec and current (μA) is shown in the curve (1) of drawing 1 by making a glassy carbon (glassy carbon) into an operation pole using this organic electrolytic solution. Here, current value can consider that the potential which rises quickly is an oxidation potential. As an example of comparison, the measurement result made to be the same as that of the above is shown in the solvent which carried out equivalent mixture of the dimethoxyethane at the propylene carbonate about the electrolytic solution which dissolved LiClO_4 to the concentration of 1M at the curve (2) of drawing 1. Although in the case of a curve (2) the increase in the current value by oxidization of a solvent is seen in the 4.8V neighborhood and it turns out on this voltage that the electrolytic solution is decomposed so that clearly from drawing, about the curve (1) which is the example of this invention, the increase in the current value by the oxidative degradation of a solvent is not seen to 5.6V. Moreover, change by the temperature (degree C) of the conductivity (mS/cm) of the electrolytic solution of this invention was shown in the curve (1) of drawing 2. In addition, conductivity was measured by the 1kHz alternating current impedance method. The temperature change of the conductivity of the LiClO_4 -propylene-carbonate electrolytic solution of 1 M concentration was shown in the curve (2) as an example of comparison. With a curve (2), it turns out that conductivity is falling rapidly at the temperature of 0 degree C or less so that clearly from the result of drawing 2. Next, using the electrolytic solution of this invention, the lithium foil was used for the negative electrode, LiNiO_2 was used for the positive electrode, and the chemical cell was produced. a positive active material -- LiNiO_2 -- as 70 % of the weight and an electric conduction agent -- acetylene black -- as 25 % of the weight and a binder -- Teflon -- 5% of the weight of the included mixture which comes out of comparatively -- using the pellet, the metal lithium was used as a negative electrode, the microporosity polypropylene sheet was further used as separator, and the coin type lithium cell was created Concordance of the electrolytic solution with a cell composition member, such as a positive electrode, a negative electrode, and separator, was good, and the interior of a cell was permeated promptly. When the charge and discharge test was performed in [voltage] 3.0V-4.5V under the 1mA constant current among the room temperature using this cell, the repeat of normal electric discharge and charge was possible.

[0008]

[Effect of the Invention] It is effective in it being fully stable, when the electrolytic solution for lithium rechargeable batteries which contains the organic fluoridation ether compound which contains a fluorine element in the molecule of this invention as explained to the detail above is applied to the lithium cell which has the high voltage exceeding 4V, and a low-temperature property being good, charge-and-discharge efficiency also having it, and the charge-and-discharge property of a longevity life being acquired. [high]

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TECHNICAL FIELD

[Industrial Application] this invention is stable, without causing oxidative degradation in the voltage range which starts the nonaqueous electrolyte for lithium cells, especially exceeds 4V in a lithium rechargeable battery, and relates to the nonaqueous electrolyte for lithium rechargeable batteries which has high conductivity also in a low temperature field 0 degree C or less.

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PRIOR ART

[Description of the Prior Art] The cell which has the developed high-energy density recently consists of the alkali-metal matter as a negative-electrode active material, a transition-metals chalcogen compound as a positive active material, and the organic electrolytic solution as the electrolytic solution. Since the lithium of the chemical cell using what used the lithium or the lithium content alloy as the negative electrode, made transition-metals chalcogen compounds, such as manganese dioxide or a vanadium pentoxide, the positive active material, and dissolved alkali-metal salts, such as a lithium perchlorate and a 6 fluoride [phosphoric-acid] lithium, in organic solvents, such as a propylene carbonate or a tetrahydrofuran, or these mixed solutions as an electrolyte also in this cell as the organic electrolytic solution is an element with the smallest specific gravity with the largest and ionization tendency also in all metallic elements. There is the feature that the energy per unit weight serves as the maximum. Furthermore, the point that electric discharge and charge are repeatedly possible as an important feature of these chemical cells is mentioned. Indicating [and] that high ion conductivity can take out big current as the organic electrolytic solution used for this chemical cell, it is a well-known fact that it must be hypoviscosity. Conventionally, it uses in many cases combining the high dielectric constant solvent and hypoviscosity solvent in which high electrolyte solubility is shown as an organic solvent for the electrolytic solutions which satisfies this condition. As a typical thing used as a high dielectric constant solvent, a propylene carbonate, an ethylene carbonate, gamma-butyrolactone, dimethyl sulfoxide, the sulfolane, the acetonitrile, etc. are known, for example. A tetrahydrofuran, dimethoxyethane, the dioxolane, etc. are known as a typical thing used as a hypoviscosity solvent. The electrolytic solution prepared using these organic solvents shows high ion conductivity, and since it is hypoviscosity, it has the feature that the transference number of ion is large. Therefore, when it considers as a cell, electric capacity increases and it is thought that the chemical cell in which high current electric discharge is possible can be realized. Here, if the requirement as an organic solvent for the electrolytic solutions is arranged, dissolve (1) electrolyte by high concentration.

(2) Fully carry out ionic dissociation of the dissolved electrolyte.

(3) Have a high oxidation potential.

(4) It is hypoviscosity. The conditions of ** are needed. Although the above-mentioned solvent used as a high dielectric constant solvent satisfies the above-mentioned conditions (1), (2), and (3), and it is a high dielectric constant therefore, the conditions of the above (4) must have been satisfied in essence. Although use of a hypoviscosity solvent is needed in order to compensate this fault, the above-mentioned hypoviscosity solvent used from the former cannot satisfy the conditions of the above (3). That is, the organic solvent for the conventional electrolytic solutions was not fully stable, when it was used for the lithium rechargeable battery using the positive-electrode material which the low thing of the own oxidation potential of a hypoviscosity solvent becomes a cause, for example, exceeds 4V, and while repeating charge and discharge, the solvent caused oxidative degradation gradually, and it had a problem of the ability not to make a long-term charge-and-discharge cycle life realize. In addition, in JP,1-117838,A, the proposal of the ** fluorine alkoxy ethane used as an electrolytic-solution solvent of a lithium cell is made as conventional technology.

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EFFECT OF THE INVENTION

[Effect of the Invention] It is effective in it being fully stable, when the electrolytic solution for lithium rechargeable batteries which contains the organic fluorine-ized ether compound which contains a fluorine element in the molecule of this invention as explained to the detail above is applied to the lithium cell which has the high voltage exceeding 4V, and a low-temperature property being good, charge-and-discharge efficiency also having it, and the charge-and-discharge property of a long-life life being acquired. [high]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] As mentioned above, when the conventional electrolytic solution for lithium cells was used for a cell with the voltage beyond 4V, there was a problem that the charge-and-discharge SAIRUKU life as a cell became short.

[0004] The purpose of this invention is very stable, and hypoviscosity shows high ion conductivity under a low temperature service, the trouble in the above-mentioned conventional technology is canceled, and oxidative degradation is not caused in the voltage range exceeding 4V, but they are [it has few falls of cell capacity and] to offer the nonaqueous electrolyte for lithium rechargeable batteries with a long charge-and-discharge cycle life.

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MEANS

[Means for Solving the Problem] in order to attain the purpose of the above-mentioned this invention -- as a hypoviscosity solvent -- a group -- the nonaqueous electrolyte containing the organic solvent which consists of an organic fluorine-ized ether compound for lithium rechargeable batteries is used this invention is nonaqueous electrolyte containing a high dielectric constant solvent and a hypoviscosity solvent for lithium rechargeable batteries, and the organic fluorine-ized ether compound shown by a following formula (** 1) or (** 2) a following formula as the above-mentioned hypoviscosity solvent is used for it.

R1-O-R1 (** 1)

R1-O-R2 (** 2)

R1 [however,] in a formula (** 1) and (** 2) a formula -- a carbon atomic number -- the fluorine-ized alkyl group of 1-10 -- as for R2, the fluorine-ized alkyl group or carbon atomic number of 1-10 expresses [a carbon atomic number] the alkyl group of 1-10 By using the organic fluorine-ized ether compound shown by an above-mentioned formula (** 1) or (** 2) an above-mentioned formula as a hypoviscosity solvent of the electrolytic solution for lithium rechargeable batteries It is stable, without causing oxidative degradation also in the voltage range exceeding 4V, and hypoviscosity can show high ion conductivity under a low temperature service, and there are few falls of cell capacity and they can realize the long lithium rechargeable battery of a charge-and-discharge cycle life. Since the viscosity as a hypoviscosity solvent will be increased, the ion conductivity in low temperature (0 degree C or less) will decrease and a cell property will fall if the carbon atomic number exceeds 10, the fluoridation alkyl group and alkyl group in the organic fluoridation ether compound shown by the above-mentioned (** 1) formula and (** 2) the formula are not desirable. And the more desirable range is an organic fluoridation ether compound with which a carbon atomic number contains the fluoridation alkyl group or alkyl group of the range of 1-5. R1 set which constitutes the organic fluoridation ether compound (R1-O-R1) shown by the formula (** 1) of this invention It is the basis which replaced with the fluorine the one section or all of hydrogen of the alkyl group shown by $C_nH_{2n+1}-$, and fluoridation alkyl groups, such as CF_3- , CF_3CH_2- , $CF_3(CH_2) (2-9)-$, and $CF_3(CF_2) (2-9)-$, are specifically mentioned. Moreover, R2 set which constitutes the organic fluoridation ether compound (R1-O-R2) shown by the formula (** 2) is a basis shown by above-mentioned $C_nH_{2n+1}-$, and the alkyl group specifically shown by CH_3- , $CH_3(CH_2) (1-9)-$, etc. is mentioned. An organic fluoridation ether compound desirable as a hypoviscosity solvent of this invention is the screw (2, 2, and 2-TORIFURORO ethyl) ether compound shown by the following formula (** 3), and $CF_3-CH_2-O-CH_2-CF_3$ (** 3)

Or n-butyl - 1, 1, 2, and 2-tetrapod FURORO ethyl ether, 2, 2, 3, 3, and 3-pen TAFURORO propylmethyl ether, 2, 2 and 3, 3-pen TAFURORO propyl - 1, 1, 2, and 2-tetrapod furol ethyl ether, A 1, 1, 2, and 2-tetrapod FURORO ethyl methyl-ether, 1, 1 and 2, and 2-tetrapod FURORO ethyl ethyl ether or 1, 1, 3 and 3, and 3-pen TAFURORO-2-TORIFURORO methylpropyl methyl ether etc. is mentioned. As a hypoviscosity solvent of the nonaqueous electrolyte containing the high dielectric constant solvent and hypoviscosity solvent of this invention for lithium rechargeable batteries a group mentioned above - the lithium cell using the nonaqueous electrolyte containing an organic fluoridation ether compound

for lithium rechargeable batteries Since the rapid decline in conductivity is not seen [in / low temperature (0 degree C or less) / the oxidative degradation potential of the above-mentioned hypoviscosity solvent is high, and] It can be stabilized and used also in the high voltage range exceeding 4V, and a low-temperature property also has the feature that it is good, charge-and-discharge efficiency is also high, and the charge-and-discharge property of a longevity life is acquired.

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OPERATION

[Function] An organic fluoridation ether compound decreases the electron density on an oxygen atom for the strong electronegativity of a fluorine atom, and has the work which prevents drawing out the electron from a molecule. Specifically compared with the ether compound which consists of usual carbon, hydrogen, and oxygen, no less than about 2.0-2.5eV of ionization potentials of an organic fluoridation ether compound becomes large. Therefore, when an organic fluoridation ether compound is used as a solvent of the electrolytic solution, an electron is not drawn out in an interface with the positive active material of a high-voltage system with the strong oxidation, and oxidative degradation becomes is hard to be carried out. Furthermore, in low temperature, since there are few falls of ionic conductivity, the feature at the time of using these organic fluoridation ether compounds for the solvent of the electrolytic solution is in the place which can take out current with them also in low temperature 0 degree C or less. [there are few falls of cell capacity and big] That is, since viscosity rose rapidly while temperature falls, the ion conductivity in low temperature decreased and the conventional organic solvent had the problem that a cell property fell. On the other hand, since rapid elevation of viscosity does not arise even if temperature falls, the electrolytic solution containing the organic fluoridation ether compound of this invention has the feature that a cell property does not fall in low temperature. As an example of the organic fluoridation ether compound of this invention, as mentioned above For example, the screw (2, 2, and 2-TORIFURORO ethyl) ether, n-butyl - 1, 1, 2, and 2-tetrapod FURORO ethyl ether, 2, 2, 3, 3, and 3-pen TAFURORO propylmethyl ether, 2, 2 and 3, 3-pen TAFURORO propyl - 1, 1, 2, and 2-tetrapod furol ethyl ether, Although a 1, 1, 2, and 2-tetrapod FURORO ethyl methyl-ether, 1, 1 and 2, and 2-tetrapod FURORO ethyl ethyl ether or 1, 1, 3 and 3, and 3-pen TAFURORO-2-TORIFURORO methylpropyl methyl ether etc. is mentioned Although it is also possible to use each above-mentioned hypoviscosity solvent independently when preparing the electrolytic solution, using the organic fluoridation ether compound of these series as a hypoviscosity solvent, you may mix and use two or more sorts of solvents. It is also possible to add and use for these organic fluoridation ether compounds the organic solvent which consists of other carbon, hydrogen, and oxygen and which is generally used further again. However, independent [which carried out in this way and was prepared], or the hypoviscosity solvent of a mixed stock cannot be used as the electrolytic solution, if the solubility of supporting electrolytes, such as LiPF₆ and CF₃SO₃Li, is low and remains as it is. As ether which contains a fluorine in a molecule, although ** fluorine alkoxy ethane which is proposed in JP,1-117838,A is known, in this, the organic fluorine-ized ether compounds of this invention completely differ structurally, for example. Moreover, there is no publication about the physical properties of the electrolytic solution of the lithium cell which dissolved and prepared the supporting electrolyte to ** fluorine alkoxy ethane in the above-mentioned open official report, and it does not have even suggestion. Although the electrolytic solution of this invention mixes the above-mentioned hypoviscosity solvent to the above-mentioned high dielectric constant solvent, and the supporting electrolyte which becomes this mixed solvent from an alkali-metal salt is dissolved and being considered as the organic electrolytic solution, as for the mixing ratio of a high dielectric constant solvent and a hypoviscosity solvent, it is desirable that it is the range of 90:10 to 20:80. The reason is

that only low ionic conductivity is too shown since a supporting electrolyte does not dissolve by high concentration that the viscosity of the electrolytic solution is high in a hypoviscosity solvent being 10% or less, and sufficient ionic conductivity is not obtained, and it is 80% or more. Moreover, it is the above-mentioned supporting electrolyte. **, LiClO₄, LiAsF₆, LiBF₄ and LiAlCl₄ which are generally known, LiCF₃CO₂, LiNbF₆, LiPF₆, LiSbF₆ and LiTaF₆, LiCF₃SO₃, LiC₆F₅SO₃, Lin-C₄F₉SO₃, and Lit-C₄F₉ -- SO₃ and Li (CF₃SO₂)₃ -- C, Li (CF₃SO₂N)₂, KSCN, KI, LiCl, LiBr, etc. can be used

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EXAMPLE

[Example] The example of this invention is given to below and it explains to a detail further using a drawing. To 100ml of propylene carbonates, beforehand, at 400 degrees C, 15g, in addition after agitating on the 1st, moisture was fully removed for the molecular sieve (type 4A) heat-treated for 4 hours through the activity alumina column. 5.32g of electrolytes LiClO_4 was dissolved in 50ml of this electrolytic-solution solvent, and the organic electrolytic solution of 1 mol concentration was prepared. Here, moisture was again removed for the organic electrolytic solution which could add screw (2, 2, and 2-TORIFURORO ethyl) ether 50ml, and was agitated through the activity alumina column. The relation between the voltage (V) when sweeping voltage by 0.1 mV/sec and current (μA) is shown in the curve (1) of drawing 1 by making a glassy carbon (glassy carbon) into an operation pole using this organic electrolytic solution. Here, current value can consider that the potential which rises quickly is an oxidation potential. As an example of comparison, the measurement result made to be the same as that of the above is shown in the solvent which carried out equivalent mixture of the dimethoxyethane at the propylene carbonate about the electrolytic solution which dissolved LiClO_4 to the concentration of 1M at the curve (2) of drawing 1. Although in the case of a curve (2) the increase in the current value by oxidization of a solvent is seen in the 4.8V neighborhood and it turns out on this voltage that the electrolytic solution is decomposed so that clearly from drawing, about the curve (1) which is the example of this invention, the increase in the current value by the oxidative degradation of a solvent is not seen to 5.6V. Moreover, change by the temperature (degree C) of the conductivity (mS/cm) of the electrolytic solution of this invention was shown in the curve (1) of drawing 2. In addition, conductivity was measured by the 1kHz alternating current impedance method. The temperature change of the conductivity of the LiClO_4 -propylene-carbonate electrolytic solution of 1 M concentration was shown in the curve (2) as an example of comparison. With a curve (2), it turns out that conductivity is falling rapidly at the temperature of 0 degree C or less so that clearly from the result of drawing 2. Next, using the electrolytic solution of this invention, the lithium foil was used for the negative electrode, LiNiO_2 was used for the positive electrode, and the chemical cell was produced. a positive active material -- LiNiO_2 -- as 70 % of the weight and an electric conduction agent -- acetylene black -- as 25 % of the weight and a binder -- Teflon -- 5% of the weight of the included mixture which comes out of comparatively -- using the pellet, the metal lithium was used as a negative electrode, the microporosity polypropylene sheet was further used as separator, and the coin type lithium cell was created Concordance of the electrolytic solution with a cell composition member, such as a positive electrode, a negative electrode, and separator, was good, and the interior of a cell was permeated promptly. When the charge and discharge test was performed in [voltage] 3.0V-4.5V under the 1mA constant current among the room temperature using this cell, the repeat of normal electric discharge and charge was possible.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the voltage-current change curve of the LiClO₄-propylene-carbonate-dimethoxyethane electrolytic solution whose curve (2) a curve (1) shows the voltage-current change curve of the electrolytic solution by this example, and is an example of comparison with drawing showing the oxidation potential by the potential sweep method of the electrolytic solution illustrated in the example of this invention.

[Drawing 2] It is the graph which shows the conductivity of the LiClO₄-propylene-carbonate electrolytic solution of 1 M concentration whose curve (2) a curve (1) shows the conductivity of the electrolytic solution by this example, and is an example of comparison with drawing showing change by the temperature of the conductivity of the electrolytic solution illustrated in the example of this invention.

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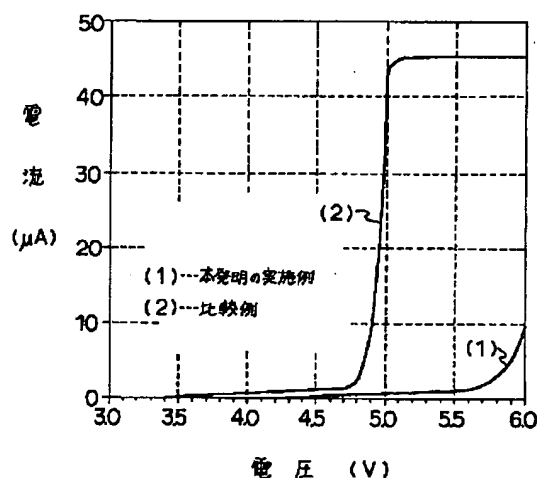
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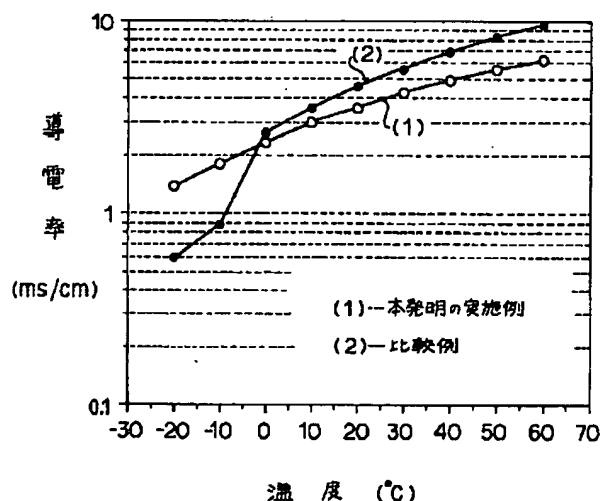
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DRAWINGS

[Drawing 1]

 1


[Drawing 2]

 2


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